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## Pressure-induced amorphization of a dense coordination polymer and its impact on proton conductivity

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## Pressure-induced amorphization of a dense coordination polymer and its impact on proton conductivity

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The proton conductivity of a dense coordination polymer (CP) was investigated under high-pressure conditions. Impedance measurements under high pressures revealed that the proton conductivity of the CP decreased more than 1000-fold at pressures of 3–7 GPa and that the activation energy for proton conduction almost doubled compared with that at ambient pressure. A synchrotron X-ray study under high pressure identified the amorphization process of the CP during compression, which rationally explains the decrease in conductivity and increase in activation energy. This phenomenon is categorized as reversible pressure-induced amorphization of a dense CP and is regarded as a demonstration of the coupling of the mechanical and electrical properties of a CP. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4898806>]

Coordination polymers (CPs) and metal-organic frameworks (MOFs) are an intriguing class of materials constructed of various metal ions and bridging ligands via coordination chemistry.<sup>1–4</sup> Their rich tunability with respect to structure and chemical composition enable a wide range of functionality of these materials, such as the ability of the adsorption and separation of gases. Among these functions, proton conductivity has begun receiving attention as another useful property of CPs and MOFs. Proton-conducting materials, exemplified by Nafion, CsHSO<sub>4</sub>, etc., are important because they function in fuel cells; in addition, numerous proton-conductive CPs have been reported for both hydrous and anhydrous systems.<sup>5–8</sup>

In addition to materials development for improved proton conductivity, the characterization of proton conduction from a more scientific and fundamental perspective is important to understanding and controlling the conductivity of these materials. One example of such research is the exploration of pressure-dependent proton conductivity; the proton conductivity and associated activation energy of various solid-state proton conductors, including clays,<sup>9</sup> oxides,<sup>10,11</sup> and cesium oxyacids,<sup>12</sup> were investigated under various pressures. In general, the aforementioned compounds tended to exhibit lower proton conductivities when under an applied pressure of the order of a few GPa, and the effects of pressure on the activation energy, activation volume, and conduction mechanism were discussed.

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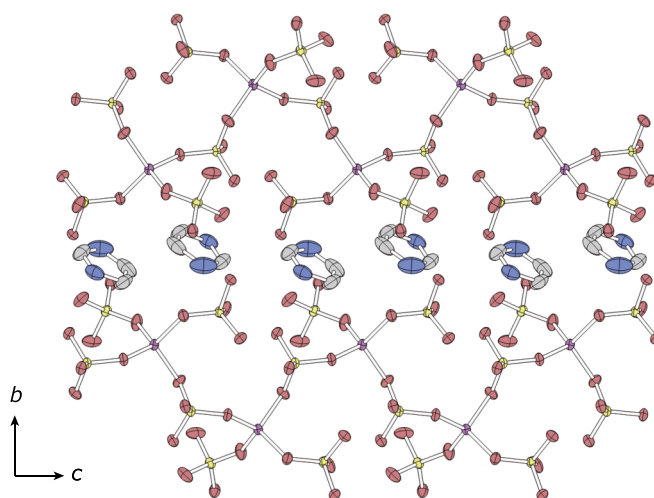


FIG. 1. Crystal structures of **1** (ORTEP 70% probability) at  $-30^{\circ}\text{C}$ . The Zn, P, O, N, and C atoms are shown in purple, yellow, red, blue, and gray, respectively. The H atoms have been omitted.

With respect to proton-conductive CPs and MOFs, however, to the best of our knowledge, studies related to pressure-dependent conductivity have yet to be performed, despite the increasing number of reports on the *de novo* synthesis of proton-conductive CPs and MOFs. In view of recently published studies on the mechanical properties of CPs and MOFs,<sup>13,14</sup> an investigation of the proton conductivity of CPs under pressure, combined with *in situ* characterization of their structures, would be interesting. Since CPs and MOFs exhibit unique responses to physical and chemical pressures because of their flexible coordination-bond architectures, the proton conductivity of these compounds under pressure is expected to highlight their characteristics. Herein, we report a study on a proton conductive CP,  $\{[\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2] \cdot 2\text{H}_2\text{im}\}_n$  (hereafter **1**; im: imidazolate), under high pressure. The influence of pressure on the proton conductivity and activation energy was characterized by *in situ* X-ray diffraction, linking the mechanical properties of CP with its functional properties.

The CP (**1**) was synthesized by the same method as previously described.<sup>15</sup> It is a crystalline CP that comprises zinc, phosphate, and imidazolium ions. Its structure contains three crystallographically distinct phosphate groups: one bridges two zinc ions, whereas the other two are monodentate to a zinc ion. Thus, the zinc ions and phosphate ligands form a one-dimensional coordination chain that is anionic, and the imidazolium molecules occupy the interspace of these chains as cations (Fig. 1). Since **1** is synthesized under an acidic condition, the phosphate and imidazolium contain acidic hydrogen atoms. These protonic parts are hydrogen bonded to each other, resulting in the formation of an extended hydrogen-bond network that serves as a proton conduction pathway. The value of proton conductivity is  $1.3 \times 10^{-4} \text{ S cm}^{-1}$  at  $100^{\circ}\text{C}$  at ambient pressure, with an activation energy of 0.47 eV. The crystal structure is dense and nonporous in the sense that it does not exhibit an adsorption property for any gases; therefore, the proton conductivity of **1** is intrinsic in Grotthuss fashion, without the aid of water molecules.

The pressure dependency of the proton conductivity of **1** was measured with a cubic-anvil high-pressure apparatus known as the DIA at  $100^{\circ}\text{C}$  (see Fig. S1(a) of the supplementary material<sup>16</sup>). We calibrated the pressure by measuring pressure-dependent electronic conductivity of bismuth metal prior to the measurement of **1**.<sup>17</sup> By connecting the high-pressure apparatus to an impedance analyzer, we obtained impedance signals of **1** as Nyquist plots (Fig. 2(a)). The conductivity calculated on the basis of the Nyquist plots is shown in Fig. 2(b) as a function of pressure. The conductivity of **1** decreased as pressure increased from ambient to 3 GPa, and then remained almost constant from 3 to 6 GPa. At pressures beyond 6 GPa through 7 GPa, the conductivity slightly increased. The activation energy for the proton conduction at 7 GPa was calculated as 0.81 eV on the basis of its temperature dependency (Arrhenius plot, Fig. 3); this activation energy is almost twice as high as that at ambient pressure (0.47 eV). The decrease in conductivity in the pressure range between 2 and 3 GPa, and the increase

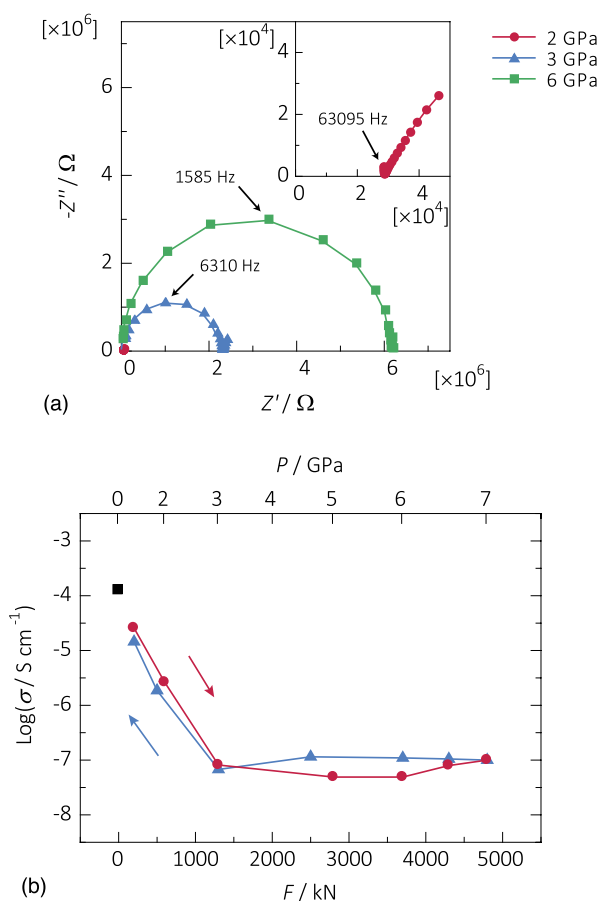


FIG. 2. (a) Nyquist plots of **1** at 100 °C under pressures of 2 GPa (red circles), 3 GPa (blue triangles), and 6 GPa (green squares) in a frequency range from 1 Hz to 1 MHz. (b) Proton conductivity of **1** at 100 °C under various pressures. Red circles and blue triangles represent increasing and decreasing pressures, respectively. The proton conductivity at 100 °C at ambient pressure is indicated by the black square as reference.

in activation energy at 7 GPa indicates that a significant change occurs in the structure of **1** while it is compressed. However, the descending process (i.e., conductivity measurements with decreasing pressure) traced the ascending process (Fig. 2(b)), and the powder X-ray diffraction (PXRD) pattern of **1** after the sample was pressed is identical to that of as-synthesized **1** (see Fig. S2 of the supplementary material<sup>16</sup>). Therefore, the effect on **1** induced by pressure is suggested to be reversible and is not preserved after the pressure is released.

For the *in situ* structural analysis of **1** under high pressure, we used a Kawai-type multianvil apparatus (see Fig. S1(b) of the supplementary material<sup>16</sup>) with synchrotron X-ray irradiation at SPring-8 (SPEED-1500).<sup>18</sup> The diffraction was measured as an energy-dispersive profile using white X-ray detected at  $2\theta = 4.0^\circ$ . We calibrated the applied pressure by measuring the XRD of Au/MgO as a pressure marker to each measurement of **1**.<sup>19</sup> At ambient pressure, the diffraction of **1** matches well with the pattern simulated from its crystal structure; however, a pressure loading of even less than 0.1 GPa ( $0.02 \pm 0.06$  GPa) caused an observable change in the diffraction pattern (Fig. 4). Although the main Bragg peaks were preserved, they all became broader than those in the pattern collected under ambient pressure. In addition, diffuse scattering from a noncrystalline (amorphous) phase increased, as indicated by the broad background in the range from 40 to 90 keV. The amount of amorphous phase increased by 43%, as calculated by estimating the diffuse scattering area from the amorphous phase with the Reflex module of the MATERIALS STUDIO 6.1 software. These results indicate that, even though **1** is a dense coordination framework, its structure is sufficiently “soft” to respond to a slight pressure of less than 0.1 GPa. As shown in Fig. 4, the Bragg peaks of **1** gradually became broader and shifted

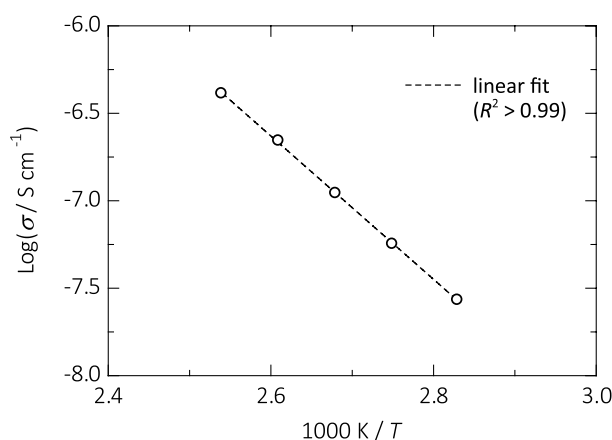


FIG. 3. Arrhenius plot of the proton conductivity of **1** from 80 °C to 120 °C at 7 GPa.

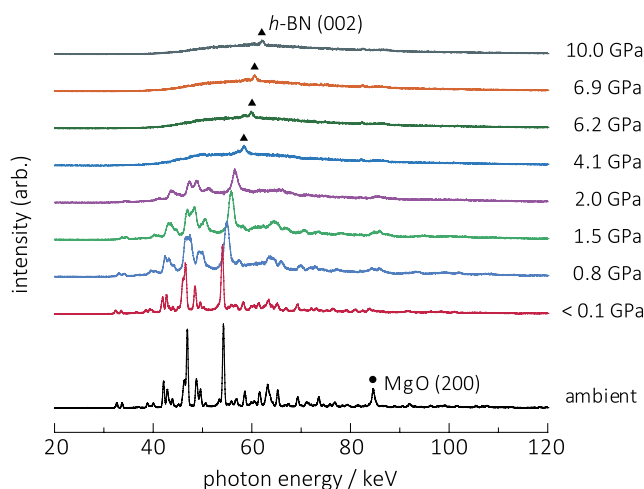


FIG. 4. Pressure-dependent energy-dispersive X-ray diffraction patterns of **1** at 25 °C.

to higher energy (smaller  $d$ -spacing) as the pressure was increased, accompanied by an increase in the area of diffuse scattering. At 4.1 GPa, the Bragg peaks from **1** disappeared, amorphization completed, and no further change was observed up to 10.0 GPa. Accordingly, this phenomenon is the reversible pressure-induced amorphization (PIA)<sup>20</sup> of **1**, by which the dense structure of **1** transforms into a more dense amorphous structure. The PIA of **1** is suggested to strongly influence the proton conductivity.

With regard to the relation between structural order and ion conductivity, the literature contains several reports that apparently contradict each other; some authors have claimed that amorphous phases exhibit better conductivity than crystalline phases,<sup>21,22</sup> whereas others contradict them.<sup>23,24</sup> Given that ion conduction is such a complicated phenomenon, in which numerous factors (number and mobility of carriers, distance between hopping sites, etc.) interplay, and that this issue has arisen for materials ranging from chalcogenides to organic polymers, categorization of such materials as good or poor ion conductors simply based on their degree of structural order (crystalline or amorphous) is difficult. Nonetheless, the conductivity of **1** can be correlated with amorphization. PIA leads to a more dense structure than that of a crystal at ambient pressure; therefore, in case of **1**, amorphization not only disturbs the uniform proton chemical potential but also reduces the amount of room available for atomic displacement and molecular motion. Since rotational motion of the imidazolium cation in **1** plays an essential role in proton conduction,<sup>15</sup> PIA impairs the conductivity of this material. The elevated activation energy also suggests that proton conduction becomes less feasible when



**1** is compressed because of creation of trapping sites and/or lack of molecular motion for a better reorganization.<sup>25</sup>

The proton conductivity of **1** increased from 6 to 7 GPa, although the XRD pattern did not change in this pressure region. Although this increase is difficult to rationalize on the basis of the data presented here, the literature contains several reports of increasing proton conductivity with pressure, which is reportedly caused by an increase in the ratio of free protons to total hydrogen atoms while a material is compressed.<sup>26</sup> Actually, a neutron diffraction study of ice (VII) indicated that some of the protons in the water molecules become detached under a high-pressure condition.<sup>27</sup> The presence of protons “squeezed” under high pressure might explain the increase in conductivity of **1** at pressures over 6 GPa.

Compared with the PIA of porous CPs and MOFs,<sup>28,29</sup> that of dense frameworks has not been extensively studied. However, PIA of dense materials is not a rare phenomenon. As examples, ice (I)<sup>30</sup> and  $\alpha$ -quartz<sup>31</sup> are known to undergo irreversible PIA;  $\text{SnI}_4$ <sup>32</sup> and  $\alpha$ - $\text{AlPO}_4$ <sup>33</sup> undergo reversible PIA. The amorphization pressure of **1** (~4 GPa) is relatively low compared with those of the aforementioned materials. The chemical variability of CPs and MOFs will offer systematic understanding and control of the PIA of dense frameworks. Thus, our results here indicate the potential for developing a tunable pressure marker that can be calibrated on the basis of electrical conductivity. Further correlation of the functional properties of CP/MOFs with physical amorphization would be an interesting research target.

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